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A modified approach for estimating the aquatic critical load of acid deposition in northern Saskatchewan, Canada

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HIGHLIGHTS

- Empirical SSWC relationships did not hold for lakes in northern Saskatchewan.
- An alternate method for SSWC critical load determination was employed.
- Accurate atmospheric deposition is needed to reduce uncertainty in CL and runoff.
- Sulphur retention appears to be an important feature in many catchments.

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ABSTRACT

Acid-sensitive ecosystems are found in northern Saskatchewan, which lies downwind of major sulphur (S) and nitrogen (N) emissions sources associated with the oil sands extraction industry. In order to protect these ecosystems against acidification, tolerance to acid deposition must be quantified. The suitability of the central empirical relationship used in the Steady-State Water Chemistry (SSWC) model to predict historical sulphate (SO_4) concentrations was investigated, and an alternate approach for determining aquatic critical loads of acidity (CL(A)) was employed for the study lakes (n = 260). Critical loads of acidity were often low, with median values of 12–16 $mmol_c\ m^{-2}\ yr^{-1}$, with the lower value reflecting a region-specific limit for acid-neutralizing capacity identified in this study. Uncertain levels of atmospheric deposition in the region, however, are problematic for characterizing acidification risk. Accurate S and chloride (Cl) deposition are needed to identify catchment sources (and sinks) of these elements in the new approach for CL(A) calculation. Likewise, accurate depiction of atmospheric deposition levels can prove useful for evaluation of lake runoff estimates on which estimates of CL(A) are contingent. While CL(A) are low and exceedance may occur according to projected increases in S deposition in the near-term, S retention appears to be an important feature in many catchments and risk of acidification may be overstated should long-term S retention be occurring in peatlands.

1. Introduction

The issue of acid rain is a long-standing global concern. In Canada, elevated deposition of sulphur (S) and nitrogen (N) to natural ecosystems across large areas has been well documented (Environment Canada, 2004). In southeastern Canada, widespread damage to acid-sensitive systems was observed (Beamish and Harvey, 1972; Duchesne et al., 2002; Watt, 1987). International efforts to reduce emissions of acid precursors during the 1980s and 1990s, including the Acid Rain Control Program (1985) and Canada-U.S. Air Quality Agreement (1991), were successful and subsequent improvements in water chemistry of affected lakes have been observed, although increases in alkalinity and pH have lagged behind decreases in lake sulphate (SO_4) concentration (Jeffries et al., 2003; Whitfield et al., 2006).

Over the past twenty years, the steady-state critical load (CL) concept has been applied to assess acid-sensitivity of aquatic and terrestrial ecosystems of Canada. The critical load of acidity (CL(A)) is the maximum load of acid deposition below which damage to sensitive biota will not occur over the long-term (Nilsson and

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Grennfelt, 1988). During the 21st century, much of the focus on acid rain in Canada has shifted to western provinces (e.g. Aherne and Shaw, 2010). While the western part of the country does not have the same historical legacy of pollution from acid deposition as the east, except in local areas around smelters, significant sources of S and N to the atmosphere associated with transportation and natural resource extraction are emerging in some areas. Critical load studies in the western provinces (e.g. British Columbia: Mongeon et al., 2010; Alberta: Whitfield et al., 2010b, Saskatchewan (SK): Scott et al., 2010; Manitoba: Jeffries et al., 2010) commonly identified acid-sensitive terrain (lakes or upland forest soils).

In Canada and around the world, aquatic CL(A) are most often determined using the Steady-State Water Chemistry model (SSWC: Henriksen and Posch, 2001). For lakes in northern SK, which are downwind of major emission sources of S and N associated with the oil sands industry, previous investigations of CL(A) indicated widespread acid sensitivity. The fifth percentile aquatic CL(A) was estimated to be <6 $mmol_c\ m^{-2}\ yr^{-1}$ (Scott et al., 2010; Jeffries et al., 2010). Improved understanding of CL(A) in northern SK is critical, as even small uncertainties could have important consequences. Likewise, poorly quantified atmospheric acid deposition could lead to large inaccuracies when determining exceedance of the CL(A). Given the acid-sensitive nature of large numbers of lakes in the region, small changes in deposition could have a significant impact.

The principles underlying the SSWC are robust and widely applicable; however, the way in which the model is typically applied is premised on empirical relationships for lakes in northern Scandinavia (Henriksen and Posch, 2001). These relationships are known to vary among regions of northern Europe, but nonetheless the SSWC has been used widely in Canada assuming empirical relationships (for Norway) are relevant across this large and geographically diverse country. It remains unknown whether these relationships are appropriate for boreal (or other) lakes in Canada. Likewise, owing to dependence of the SSWC on observations of surface water chemistry and the assumption that SO_4 is mobile, one complicating factor when calculating CL(A) can be catchment sources (or sinks) of SO_4. Sulphur biogeochemistry is complex, for example as conversion of the mobile SO_4 ion to organic S or sulphides can result in retention. Sources and sinks of SO_4 are often not considered, however appropriate modifications are required in instances where they occur. In the case of chloride (Cl), failure to identify local sources can also be problematic, as correction of base cation concentrations to a non-marine component can produce irreconcilable results (negative concentrations).

The central objective of this study was to improve the capacity for estimating CL(A) by considering alternate approaches for SSWC application, and to describe the uncertainty in CL(A) exceedance using available atmospheric deposition estimates. Modelled atmospheric deposition (total S, N, Cl and base cation (BC)) and lake chemistry data for 260 headwater lakes in northwestern SK were used to characterize their acid sensitivity and determine the risk of acidification. As N is a limiting nutrient in terrestrial systems of the region and lake N is very low, the focus of the study was S. As part of the study, the empirical regression approach used in SSWC for estimating historical SO_4 concentrations was tested for the first time outside Europe. Refinements for SSWC application were considered, and a new approach for SSWC application is presented.

2. Methods

2.1. Study area and data sources

Northwestern SK features a subarctic climate with a combination of snow and rain precipitation, and strongly varying seasonal temperatures. Long-term annual precipitation is between 450 mm and 530 mm, with mean temperatures of approximately 16 °C in July and −24 °C in January (Environment Canada, 2015). The study area traverses three boreal ecoregions: Athabasca Plain (AP), Churchill River Upland (CRU), and Mid-Boreal Upland (MBU); all of which vary in soil type, vegetation, regional geology, and geographic landforms. Candidate headwater lakes (10–400 ha) within 300 km of the centre of the oil sands industry near Fort McMurray, Alberta (Fig. 1) were identified in alternating polygons delineated using 10° azimuth angle increments intersected at 25 km radial intervals. The study lakes (n = 260) were chosen randomly from the candidate pool and sampled for water chemistry during fall turnover in one or more years (2007, 2008, 2009, 2011). Further details on sample collection, analytical methods and the study area can be found in Scott et al. (2010). Lake runoff estimates according to the isotope mass balance method (Q_{imb}), and a grid-based method (Q_{grid}) were used. The isotope mass balance method takes into account site-specific hydrology, while the grid-based method represents average precipitation surplus within a 0.5° (latitude by longitude) grid (Gibson et al., 2010). Mineral soils in the region are generally well-drained (in particular for boreal shield ecoregions (AP and CRU)); deposits are largely glaciolacustrine or glaciofluvial till overlaying crystalline Precambrian bedrock. Upland forest soil plots (n = 73) were sampled across the study area (in the same ecodistricts (ecoregion subdivision) as study lakes) and analysed according to Whitfield and Watmough (2012).

2.1.1. Atmospheric deposition

Estimates of atmospheric deposition were used in the alternate approaches for estimating CL(A) for lakes, and for identifying acidification risk. In boreal and taiga regions of Saskatchewan deposition data from monitoring programs are very limited, leading to poorly documented regional deposition patterns. Sulphur deposition was estimated according to the on-line chemical transport model GEM-MACH run for meteorological year 2013 (Makar et al., 2015). Estimates of mapped wet (Ro and Vet, 2003) and dry (Vet and Shaw, 2004) BC and Cl deposition for the period 1994–1998 interpolated to a common grid resolution for total deposition were available for the study catchments; these data were required in the alternate approach for SSWC application described below.

2.2. Critical loads of acidity

2.2.1. Steady-state water chemistry model

The Steady State Water Chemistry (SSWC) model (Henriksen and Posch, 2001) can be used to calculate CL(A) in an empirical fashion using water chemistry and runoff data. The CL(A) was calculated for each study lake with sea-salt corrections for SO_4 and BC (calcium (Ca), magnesium (Mg), potassium (K), and sodium (Na)) concentrations in lakes. Observed lake Cl is used for sea-salt corrections, with correction factors of 0.104 for SO_4, 0.04 Ca, 0.21 for Mg, 0.86 for Na and 0.109 for K (Evans et al., 2001). Where multiple observations were available, the average lake chemistry condition was used to calculate the CL(A):

$$CL(A) = ([BC^*]_0 - ANC_{limit}) \times Q_{imb} \quad [1]$$

where Q_{imb} is the site-specific watershed runoff (m y^{-1}), and $[BC^*]_0$ is the sea-salt corrected (denoted by *) pre-acidification BC concentration. Lake-specific ANC_{limit}, the lowest (charge balance) acid neutralizing capacity (ANC) above which biota do not respond adversely, was set to 10 $\mu mol_c\ L^{-1}$ (Scott et al., 2010), then scaled to account for organic acidity according to Lydersen et al. (2004):

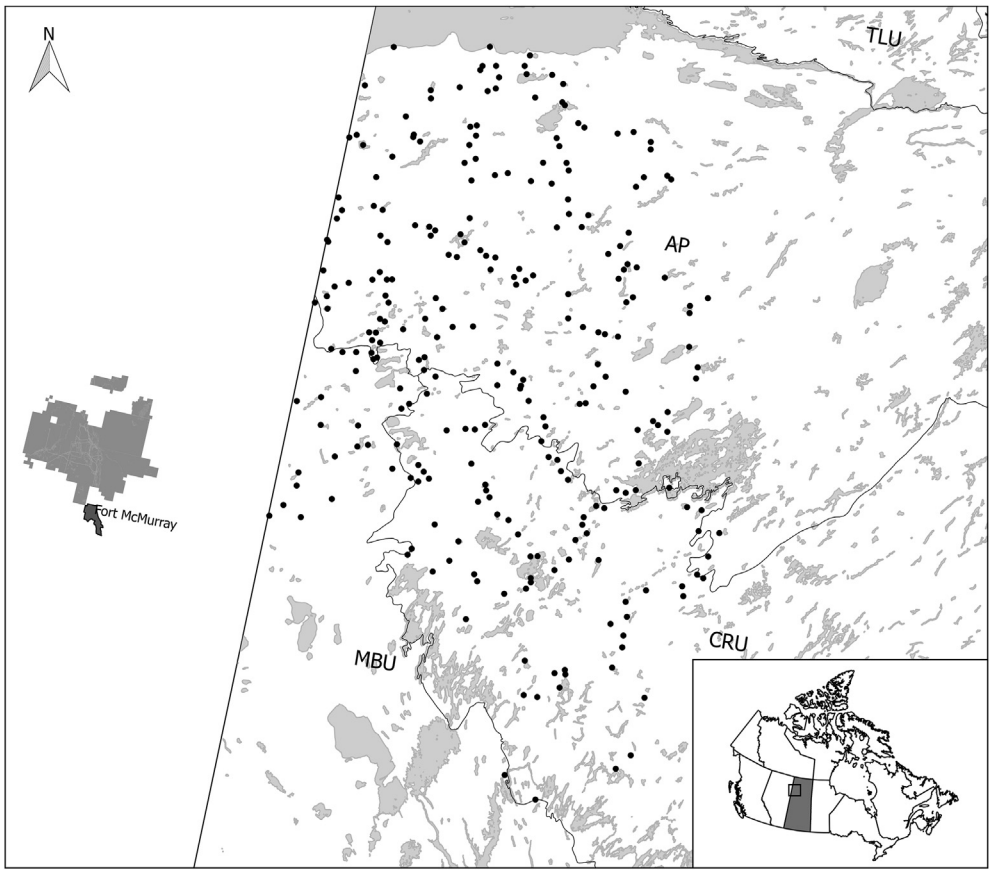

Fig. 1. Location of the study lakes (black circles) in the Athabasca Plain (AP), Churchill River Upland (CRU) and Mid-Boreal Upland (MBU) ecoregions of Saskatchewan. The province of Saskatchewan is shown as grey polygon in inset map of Canada. The town of Fort McMurray (dark polygon) and Oil Sands mining areas north of the town are shown to the west of the study lakes in the province of Alberta.

$$ANC_{limit} = 10 + \frac{10.2}{3} \times [DOC] \quad [2]$$

where 10.2 $\mu mol_c\ mg^{-1}$ represents site density (for organic carbon), and [DOC] is the concentration of dissolved organic carbon (DOC) present in the lake (mg C L^{-1}). This approach of setting a lake-specific ANC_{limit} is not typical of all SSWC studies in Canada, but has been commonly employed in recent years. In cases where observed ANC adjusted for strong organic acids (ANC_{oa}: Lydersen et al. (2004)) was less than ANC_{limit}, ANC_{limit} was set equal to ANC_{oa} which avoids negative (meaningless) CL(A). Using the sum of present day base cations, $[BC^*]_t$, $[BC^*]_0$ can be estimated using the F-factor:

$$F = \sin\left(\frac{\frac{\pi}{2} \times Q_{imb} \times [BC^*]_t}{S}\right) \quad [3]$$

$$[BC^*]_0 = [BC^*]_t - F\left(\left[SO_4^*\right]_t - \left[SO_4^*\right]_0 + [NO_3]_t - [NO_3]_0\right) \quad [4]$$

The constant S, the base cation flux at which F = 1, has been estimated from studies in Norway to be 400 $mmol_c\ m^{-2}\ y^{-1}$. Nitrate concentrations were very low and played a negligible role. Pre-industrial non-marine sulphate, $[SO_4^*]_0$, reflects a background contribution from atmospheric deposition (intercept), and a geologic contribution that is scaled from BC concentration:

$$\left[SO_4^*\right]_0 = 8 + 0.17 \times [BC^*]_t \quad [5]$$

The coefficients are based on Norwegian lakes receiving less than 16 $mmol_c\ m^{-2}\ yr^{-1}$ of S deposition; the equation was chosen for use herein as it exhibited the highest correlation coefficient among reported regressions (see Henriksen and Posch, 2001) and has been used for previous studies in Canada.

2.2.2. Sulphate correction

An alternate SSWC method which uses a modified series of equations to account for high SO_4 concentrations due to (geological) weathering was described by Závodský et al. (1996). This method was applied at all catchments that exhibited SO_4 sources. The difference between modeled 2013 S deposition concentration adjusted for evapotranspiration losses of water (SO_{4dep}) and lake concentration (SO_{4t}) is assumed to originate from geologic sources, with equivalent amounts of BC assumed to originate from S bearing minerals (BC_{geol}).

$$BC_{geol} = SO_{4t} - SO_{4dep} \quad [6]$$

This geologically supplied BC was then compared to runoff BC concentration (BC_t) to find the present base cation concentration from weathering and deposition sources (BC_{wt}), all expressed as $\mu mol_c\ L^{-1}$:

$$BC_{wt} = BC_t - BC_{geol} \quad [7]$$

It should be noted that there is no functional difference between BC_{geol} and BC_{wt}; the purpose of unique terms is to identify BC available to buffer atmospherically derived acid deposition. The F-

factor is described using a modified equation, defined as the change in BC_{wt} concentration due to a change in SO_4 concentration:

$$F = \frac{BC_{wt}}{S} \quad [8]$$

A default value of 4000 $\mu mol_c\ L^{-1}$ is used for S in this method. This differs from the (flux-based) value used above, as in this case BC_{wt} and S used to calculate F are expressed in concentrations. Historical base cation concentration (BC_0) was calculated as:

$$BC_0 = BC_{wt} - F \times SO_{4dep} \quad [9]$$

where as a simplification, all SO_4 deposition was assumed to be anthropogenic. Historical base cation concentration was adjusted to the non-marine fraction using observed Cl concentration and used to calculate CL(A) according to Equation (1).

2.2.3. Baseline approach

A simplified approach to CL(A) calculation, premised on the assumption that the study lakes have not yet experienced significant changes in chemistry due to atmospheric deposition, and accounting for catchment sources of both SO_4 and Cl was also used. Building on the approach presented by Závodský et al. (1996) for SO_4, catchment sources of Cl were identified using deposition and surface water data. Modelled deposition fluxes to the lake catchments were compared against the observed (present day) amount of Cl export ($mmol_c\ m^{-2}\ yr^{-1}$). Where Cl export (determined from Cl concentration and annual runoff) is greater than the deposition Cl flux, excess Cl was assumed to originate from within the catchment and converted to a concentration ($[Cl]_{Source}$). For lakes where sources were identified, an adjusted lake Cl concentration ($[Cl]_{atm}$; $\mu mol_c\ L^{-1}$) was determined from Cl deposition and Q_{imb}. This adjusted Cl concentration due to atmospheric deposition was assumed to reflect marine Cl. Sulphate sources for the catchment were also determined by comparing deposition and lake export, with excess SO_4 assumed to be time-invariant and of catchment origin and converted to a concentration ($[SO_4]_{Source}$). The lake catchments are remote, and there are no local sources of pollution (e.g. road salt) that could result in sources of S and Cl at individual catchments; the closest major source of atmospheric pollution being north of Fort McMurray, Alberta (Fig. 1).

By assuming that the observed conditions represent a relatively undisturbed or baseline state of the lakes, a modified SSWC approach can be used to calculate the CL(A):

$$CL(A) = ([BC^*]_t - [Cl]_{Source} - [SO_4]_{Source} - ANC_{limit})Q_{imb} \quad [10]$$

where the observed base cation concentration of non-marine origin $[BC^*]_t$ is determined using $[Cl]_{atm}$.

2.3. Uncertainty and exceedance

Uncertainty in the baseline estimates of CL(A) was quantified. To characterize the uncertainty in CL(A) due to BC_t, and Q_{imb}, 1000 simulations (each) were performed for each lake using BC_t and Q_{imb} values randomly selected from parameter-specific distributions. The BC_t values were selected from a normal distribution within one standard deviation of the mean. For lakes where only a single observation was available, the average relative standard deviation of lakes with multiple observations was used. Error attributable to Q_{imb} was calculated assuming 20% error for the upper and lower limits of a uniform distribution. After describing uncertainty in BC_t, or Q_{imb}, Equation (10) was used to characterize uncertainty in CL(A) due to each parameter for each lake (n = 260). Combined uncertainty in CL(A) was quantified by simultaneous selection of Q_{imb} and BC_t values from distributions described above (10,000 iterations used).

For the baseline method, the underlying assumption is that lakes are in approximate steady-state with no appreciable anthropogenic S. Therefore, an estimate of future increase in S deposition was used to (conservatively) explore the potential for exceedance of the CL(A), with current S deposition not contributing to exceedance. Sulphur deposition in the region was projected to increase 15% over the 2000–2020 period (Environment Canada, 2004). Assuming a linear increase during this period, a 5% increase above the 2013 deposition estimates could be expected; this increase was used to characterize the potential for exceedance in the near future.

2.4. ANC_{limit}

The ANC_{limit} (Equation (2)), is often defined according to the response of fish, and in particular Brown Trout (*Salmo trutta*) (Lydersen et al., 2004). Using Brown Trout population damage as a chemical indicator for northwestern Saskatchewan lakes is imperfect in a traditional sense because Brown Trout, while an exemplar acid-sensitive salmonid species, are non-native and absent (except in very occasional stocking situations). Native fish species common to northwestern Saskatchewan lakes are Lake Trout (*Salvelinus namaycush*) in larger, deeper lakes and Northern Pike (*Esox lucius*) which are widely distributed. Walleye (*Sander vitreus*) and Whitefish (*Coregonus clupeaformis*) are also important harvest species in the study region; Whitefish are less sensitive to acidity than trout (Lien et al., 1996). Based on data for Norway (Lien et al., 1996), with a fixed ANC_{limit} of 10 $\mu mol_c\ L^{-1}$ Northern Pike would be expected to experience ~24–28% reduction in population, as well as potential risk of extirpation from individual lakes (Lien et al., 1996). In contrast, at a fixed ANC_{limit} of 25 $\mu mol_c\ L^{-1}$, minimal reduction in population size of Northern Pike and other species is anticipated. Therefore, an ANC_{limit} (25 $\mu mol_c\ L^{-1}$) that is more protective of native fish species than what has been used previously (Scott et al., 2010; Jeffries et al., 2010) may be preferred.

Furthermore, of the 260 lakes, 53 are (naturally) fishless (Anas et al., 2015) and thus, an ANC_{limit} based on invertebrate tolerances to acidic conditions would be more appropriate. A pH of 6 was identified as the threshold for zooplankton community change in softwater lakes of the eastern Canadian boreal shield (Holt et al., 2003). Regression of pH and ANC among the study lakes indicates that an ANC_{limit} of 40 $\mu mol_c\ L^{-1}$ is relevant for the pH threshold of 6. Accordingly, zooplankton appear to be more sensitive to changes in water chemistry than fish species, and this more protective alternate ANC_{limit} may be necessary to protect the ecological integrity of all study lakes and not only those where fish are absent. Critical loads and exceedance were investigated using the default (10 $\mu mol_c\ L^{-1}$) and alternate (40 $\mu mol_c\ L^{-1}$) ANC_{limit} values with both scaled for organic acidity according to Equation (2). As described above, where ANC_{oa} was less than the calculated ANC_{limit}, ANC_{limit} was set equal to ANC_{oa}.

3. Results and discussion

3.1. Chemical characteristics

The headwater study lakes span a range of chemical character (Table 1). In general the lakes are circum-neutral to slightly acidic, with approximately 25% of the lakes having pH greater than 7. Base cation concentrations range from <50 to upwards of 2000 $\mu mol_c\ L^{-1}$, with Ca being the dominant cation. Sulphate concentrations are highly variable but consistently lower than BC concentrations. Dissolved organic carbon is generally high, with

Table 1
Lake chemistry and atmospheric deposition characteristics for the study lakes (n = 260). 5th percentile, median, mean, and 95th percentile values are shown for pH, charge balance acid neutralizing capacity adjusted for strong organic acids (ANC_{oa}), base cation (BC), chloride (Cl), inorganic nitrogen ($NH_4 + NO_3$), sulphate (SO_4) and dissolved organic carbon (DOC) concentrations, and chloride (Cl_{dep}), and (2013) sulphur deposition (S_{dep}).

	pH	ANC_{oa}	BC	Cl	$N_{inorganic}$	SO_4	DOC mg L^{-1}	Cl_{dep}	S_{dep}
		$\mu mol_c\ L^{-1}$						$mmol_c\ m^{-2}\ yr^{-1}$	
5th Percentile	6.2	41	88	2.8	1.0	5.7	2.2	1.2	7.2
Median	7.0	138	184	5.2	1.9	16	6.1	1.5	9.9
Mean	7.0	229	291	19	3.4	18	7.0	1.5	10
95th Percentile	7.8	725	834	61	11	41	15	1.8	15

concentrations greater than 6 mg L^{-1} in upwards of 50% of the study lakes. Consequently, ANC can be strongly influenced by organic acids in the study region; ANC_{oa} suggests that many of the study lakes are acid-sensitive (Table 1). Scott et al. (2010) characterized low pH lakes in the region as being shallow and dilute. Furthermore, while considerable variability exists within different ecoregions, AP lakes were reported to have lower BC and bicarbonate concentrations than lakes located in the MBU. This is consistent with upland soil weathering capacity in the region, with the AP having extremely low weathering release of base cations attributed to sandy, well drained soils with very high quartz content; low to moderate weathering rates were reported for CRU and MBU soils within the study area (Whitfield and Watmough, 2012). Upland forest soils across the study area are generally coarse textured and acidic with low organic matter (Table 2). Base saturation is low, owing to low base cation content and weathering rates of the soils and S content of surficial soils is also low (Table 2).

Atmospheric Cl deposition is low, ranging from 1.2 to 1.8 $mmol_c\ m^{-2}\ yr^{-1}$ (Table 1) and generally increasing from southeast to northwest across the study region indicative of a marine influence and not hydrochloric acid deposition associated with coal burning as can be important elsewhere (Evans et al., 2011). Base cation deposition is estimated to be between 8 and 14 $mmol_c\ m^{-2}\ yr^{-1}$ in the region, with differences among catchments attributed to the influence of landcover on deposition as well as a general decrease with latitude and longitude. Sulphur (and N) deposition estimates are consistently lower than areas of southeastern Canada (Aherne and Jeffries, 2015). Maximum S deposition to the study sites was 22 $mmol_c\ m^{-2}\ yr^{-1}$ according to the most recent modeled deposition estimates (Makar et al., 2015). Sulphur deposition in the region is comparable to deposition received in northern Scandinavia during the 1980s where lake chemistry data were used as the basis for the empirical relationships (e.g. Equation (5)) in the SSWC model (Henriksen and Posch, 2001).

Comparison of deposition fluxes to the lake catchments and runoff exports (calculated using Q_{imb} and average lake concentrations) indicated a wide range in behaviour of the study lakes. Some of the lake catchments demonstrated export fluxes in excess of modeled Cl and S deposition (Fig. 2), evidence of an internal source or potential underestimate of deposition. Given the absence of any clear spatial pattern associated with the apparent Cl sources (and the retention estimated for most catchments), underestimation of deposition is unlikely as an explanation. Analyses of forest soil mineralogy in the region have not identified Cl-bearing minerals in the rooting zone. Nonetheless, sources of Cl in the region may include halite (AP, especially Carswell Plain sub-region; Scott et al., 2010), while sedimentary rocks of marine origin that are ubiquitous in the region or higher Cl content metamorphic rock could also be contributors. While more work is needed to identify the sources of Cl in surface waters draining these catchments, it is worth noting that Whitfield et al. (2010a) also identified notable sources of Cl (and S) for lakes located on similar terrain to the west of the study area. Catchments acting as a source of SO_4 (n = 14) were located near the centre of the study region where potential geological sources of S include shale, gneiss and sulphides (Tremblay, 1982).

The majority of the study catchments are sinks for Cl and S (Fig. 2). In the case of Cl, where the sinks are small, it is plausible that Cl deposition could be overestimated or runoff underestimated (see Section 3.3.below). Alternately, while Cl is generally considered to demonstrate conservative behaviour, Cl retention in the catchments may occur, for example due to plant uptake (Berger et al., 2001) and long-term storage in organic soil. Long-term storage of S is also likely to occur, as strong retention of S was evident, and relatively little atmospheric S deposition appeared in many lakes (Fig. 2). Significant long-term storage of S in peatlands has been documented elsewhere, with 18 $mmol_c\ m^{-2}\ yr^{-1}$ stored in European peatlands receiving low levels of anthropogenic S deposition, and higher storage possible where S deposition is higher or S-rich plant species are present (Novak et al., 2005). The magnitude of this sink is comparable to atmospheric S deposition in the study area (Table 1) suggesting that much of the deposition to peatlands may be retained. This appears to be the primary mechanism of S retention in the study catchments, as coarse-textured mineral soils typical of the region feature low iron and aluminium oxide content (Table 2) and demonstrate very limited capacity for S adsorption (Whitfield et al., 2010c). The catchment sinks may not be permanent in the case of S, as there is potential for episodic release of some S from near surface fibric peat during water table drawdown (Whitfield et al., 2010c). Over the long-term however, peatland dominated lake catchments nearby in Alberta have been characterized as retaining atmospherically deposited S (Whitfield et al., 2010a).

Table 2
Upland forest rooting zone mineral soil pH, organic matter (OM), cation exchange capacity (CEC), base saturation (BS), and sand, clay, silica (SiO_2) and sulphur (S) content in the study area (n = 73).

	pH	OM	CEC	BS	Sand	Clay	SiO_2	S[a]
		%	$mmol_c\ kg^{-1}$	%	%	%	%	$mg\ kg^{-1}$
5th Percentile	4.3	0.2	14.1	0.9	37.1	0	80.6	0.4
Median	4.9	0.6	49.4	6.9	84.9	1.1	96.3	1.2
Mean	4.7	1.1	67.5	9.8	77.3	2.0	93.4	2.2
95th Percentile	5.7	3.9	152	27	98.2	5.2	98.4	7.3

[a] Surface horizon only.

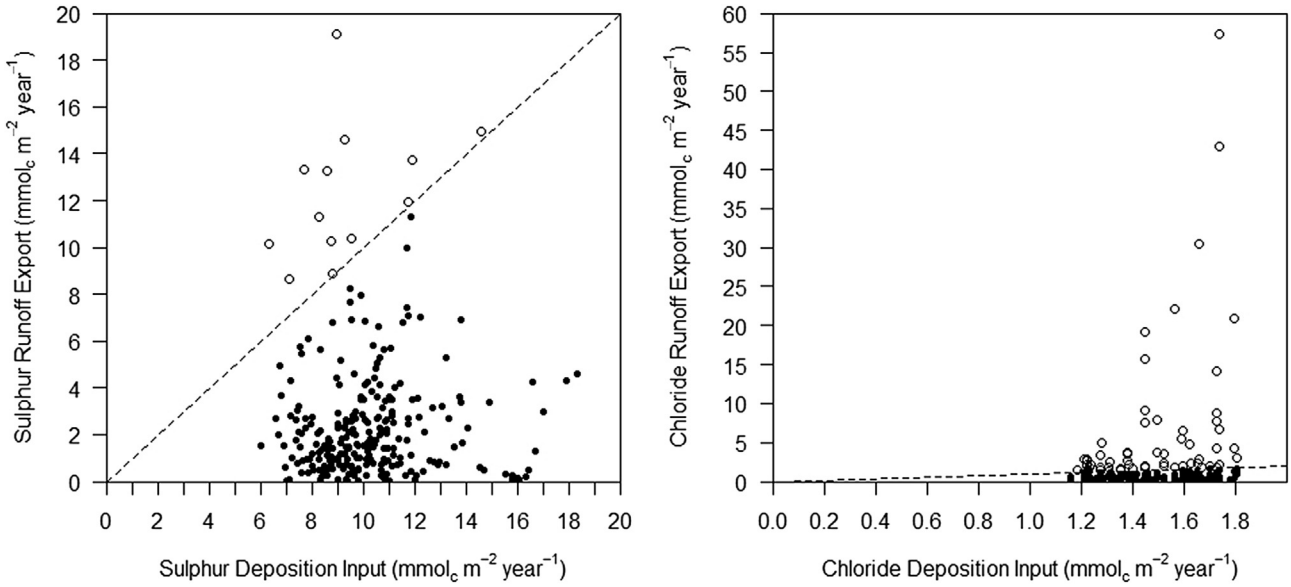

Fig. 2. Annual fluxes for sulphur (left panel) and chloride (right panel) to and from the study catchments. Input fluxes are estimated from atmospheric deposition, and export calculated using observed lake concentrations and runoff. The one to one line is shown and lakes with catchment sources are identified with open circles.

3.2. Critical loads of acidity

Critical loads of acidity were calculated using several methods. The SSWC was applied for consistency with previous applications in the region and elsewhere in Canada. This 'standard' approach to CL(A) calculation yielded values very similar those reported by Scott et al. (2010) owing to the consistency of approach (Table 3). Inclusion of one additional lake and two additional years observations yielded minor differences (slightly higher maximum value reported herein) while setting ANC_{limit} equal to ANC_{oa} in select cases resulted in a minimum CL(A) of zero. Using an approach to CL(A) calculation similar to the standard SSWC described herein, Cathcart et al. (this issue) also reported widespread acid-sensitivity among lakes of northern SK. Using corrections for internal catchment sources of S generally resulted in lower CL(A) (Fig. 3, Table 3), although few lakes exhibited notable differences consistent with the small number of catchments where S sources were identified.

One drawback of using SSWC according to the standard method described above is that a majority of predictions (Equation (5)) of pre-industrial non-marine sulphate were higher than current observations. Given the variability in this type of empirical relationship reported for other regions (e.g. Henriksen and Posch, 2001) this result is not completely unexpected, but it certainly raises the question of whether empirical relationships for boreal lakes in Scandinavia are suitable for lakes in western boreal regions of Canada. Relationships between $[BC^*]_t$ and $[SO_4^*]_t$ were investigated in an attempt to use a locally relevant regression for prediction of historical non-marine SO_4 concentration. Linear regressions for all study lakes in the region, as well as subsets for lakes in each ecoregion representing more homogeneous geological substrates, revealed no evidence of a relationship between BC and SO_4 (Fig. 4). An expanded dataset that included an additional 409 AP and CRU lakes (Jeffries et al., 2010) also failed to yield a regression with a meaningful co-efficient of determination. Likewise, when exclusively low ANC (<200, <500 μmol$_c$ L^{-1}) lakes were considered, no regionally relevant regression emerged as a candidate for characterizing historical SO_4 concentrations. In the study area, where organics are the dominant anion (Scott et al., 2010), S reduction and storage may be principally responsible for the lack of a SO_4-BC relationship. This is a strong reminder that models should not be applied outside the region for which they were developed without due consideration of underlying assumptions of key empirical relationships.

In the absence of an empirical relationship that can be reliably used to predict historical SO_4, an alternate method of CL(A) calculation was considered. This baseline method generated CL(A) that were very similar to the Standard method (Table 3, Fig. 3). Despite the different approach employed, the similarity in results can be attributed to several factors. In the standard method, observed lake Cl was used to sea-salt correct BC concentrations. Thus catchment Cl sources were accounted for, although in some instances BC were overestimated as a result of incorrect (sub-zero) predictions of individual cations from sea-salt ratios that are inconsistent with geologic sources of BC in the catchments. Predictions of historical SO_4 according to Equation (5) were generally higher than current concentrations, thus use of the F factor (Equation (4)) was unnecessary and most lakes were described according to current conditions regardless of method used. Finally, while differences in CL(A) between methods were observed for select lakes (Fig. 3), these were limited to the few cases with notable SO_4 sources. Accordingly, should the baseline method be used where a greater proportion of lakes demonstrate sources of S in the catchments (as would be the case in the current study if S deposition is overestimated or runoff underestimated), the baseline method should

Table 3
Critical loads of acidity (mmol$_c$ m^{-2} yr^{-1}) for the study lakes (n = 260) calculated according to standard, sulphate correction and baseline variations of the Steady-State Water Chemistry model (see methods for details). Critical loads for the baseline approach with an alternate ANC_{limit} are also shown.

Percentile	Standard	SO_4 correction	Baseline	Baseline alternate ANC_{limit}
0	0	0	0	0
5	1.9	1.9	1.9	0
25	7.7	7.6	7.7	4.2
50	16.5	16.4	16.4	12.3
75	38.8	38.2	38.6	31.8
95	120	115	120	106
100	344	326	331	326

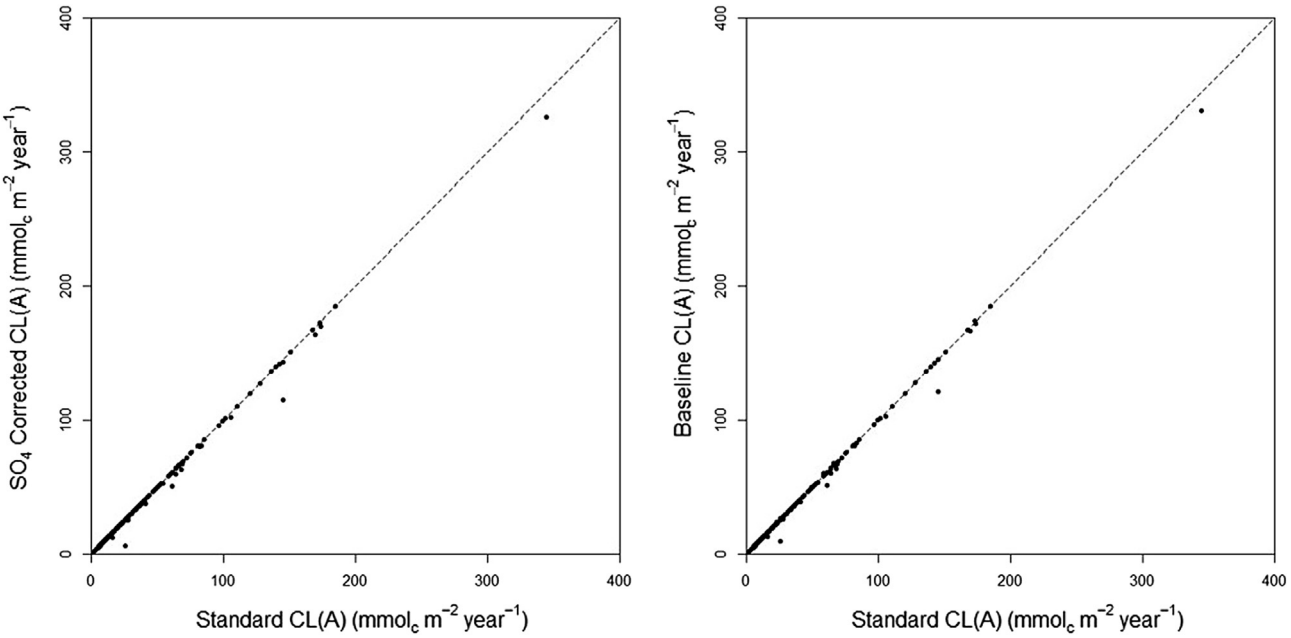

Fig. 3. Critical loads of acidity (CL(A)) calculated using variations of the Steady-State Water Chemistry model. The Standard approach (x-axis) is compared against results generated using (a) SO_4 correction and (b) Baseline approaches.

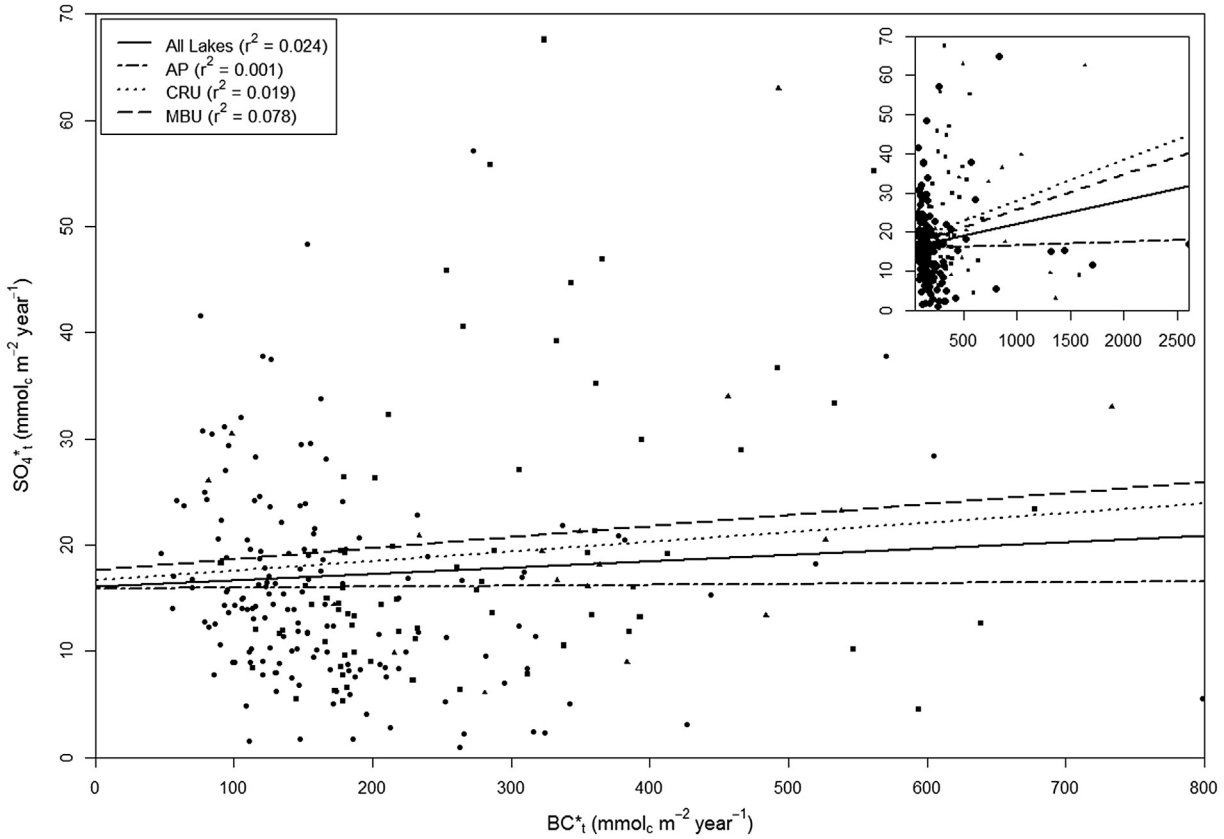

Fig. 4. Relationship between observed non-marine sulphate and base cation concentrations in the study lakes. Regressions lines are plotted for all study lakes, and each ecoregion (Mid-Boreal Upland (MBU): triangles, Athabasca Plain (AP): circles, and Churchill River Upland (CRU): squares). Inset shows full range of observations.

provide more robust estimates of the CL(A).

In addition to providing more robust estimates of CL(A) where S sources are identified, the baseline method may be preferred because it eliminates the need to predict historical SO_4 concentration (and therefore does not require arbitrary decisions about the predictions where they are inconsistent with understanding of

the system). It likewise eliminates reliance on the F factor. This is an important consideration, as the value of S used in setting the F-factor has not been tested nor have alternate values been identified for use in boreal regions of Canada. Further, current knowledge supports use of a baseline method, as acid deposition levels for the region have been relatively low during the industrial period. Sulphur deposition from the closest regional source (the Athabasca Oil Sands region) is believed to be elevated over a relatively short distance (less than 100 km) from the centre of the industrial complex (Watmough et al., 2014). Very little S from this source is expected to reach the study lakes and as demonstrated herein, much of atmospheric S deposition to these catchments does not appear in lakes. Given these considerations, the baseline approach should be viewed as a valid approach for setting the SSWC CL(A) in the study area.

Several lakes demonstrated ANC_{oa} lower than the default ANC_{limit}, and upwards of 5% had ANC_{oa} lower than the alternate limit. This highlights the importance of considering the baseline natural lake condition when setting the limit. Regardless of approach and ANC_{limit} used, SSWC CL(A) were low for many of the headwater lakes considered, with median CL(A) less than 20 $mmol_c\ m^{-2}\ yr^{-1}$ according to all approaches. It is worth noting here that the correction for organic acidity is based on site density for boreal lakes in Sweden. Site density is variable (Kohler et al., 1999; Lydersen et al., 2004), and the characteristic site density of DOC in the study lakes remains unknown. Nonetheless any error in CL(A) attributed to poorly characterized site density should be small (<3 $\mu mol_c\ L^{-1}$).

3.3. Uncertainty

By definition, the CL concept is used to represent the long-term steady-state of a system. Knowledge available with which to characterize this equilibrium condition of individual sites, however, is typically imperfect, particularly in regional assessments where long-term records are sparse. Accordingly, it is good practice to describe known uncertainties associated with critical loads, rather than rely solely on a single optimal value. Quantifying uncertainty associated with critical loads is particularly important for the assessment of deposition scenarios (Wolniewicz and Aherne, 2010) and emissions management policy.

In the current study focusing on remote lake catchments with limited observations, uncertainty associated with the baseline approach was investigated as uncertainty in BC concentrations and Q_{imb}. Uncertainty associated with the potential use of different ANC_{limit} can also be explored, but because selection of ANC_{limit} is based on both science (knowledge of the ANC levels at which changes to biotic community occur) and policy (acceptable levels of change, or designation of species to protect) this was considered separately through the use of two distinct limits (e.g. Table 3). Individually, neither uncertain $[BC^*]_t$ (Fig. 5a) nor Q_{imb} (Fig. 5b) yielded large uncertainty in CL(A). Collective uncertainty is highest for the least acid-sensitive lakes (Fig. 5c), while both the 5th and 95th percentile CL(A) are zero for the most acid-sensitive lakes.

It is worth noting that the uncertainty attributed to Q_{imb} was not based on known error in observation of Q, but rather a simplified (relative) estimate of uncertainty necessary owing to imperfect understanding of catchment hydrology in the region. Catchment-specific (Q_{imb}) estimates, while often diverging widely from regional estimates of Q (e.g. Q_{grid}), are understood to be the more reliable estimate (Bennett et al., 2008; Gibson et al., 2010). Nonetheless, while Q_{imb} estimates were available for the study catchments they could not be used with confidence for all lakes. Of the 260 Q_{imb} estimates, 11 were higher than long-term precipitation amounts (Fig. 6). Such patterns have been explained elsewhere as contributions from permafrost melt (Gibson et al., 2015). Alternately, groundwater inputs could be responsible for these observations, due to limitations of topographically-based catchment delineation (Devito et al., 2005). For the headwater study catchments considered in the current study, however, groundwater discharge originating outside the topographic divide of the catchment is an unlikely mechanism, and permafrost is not an important feature of the landscape. This apparent overestimate of runoff could instead be linked to error in catchment area used in the isotope mass balance model. Possible sources of error include resolution of the digital elevation model used to delineate catchments, or presence of non-contributing areas. Given that for some lakes, very low Q_{imb} was indicated instead (Fig. 6), hydrochemical flux calculations were used as a means of assessing these estimates. Export fluxes of Na and Cl (according to observed lake concentrations and Q_{imb} runoff estimates) were compared against modeled deposition inputs. As a conservative approach, Cl deposition was assumed to be overestimated by a factor of two and weathering contributions of Na were not considered. In cases where calculated export was less than input flux (for both elements), runoff from the lake was assumed to be underestimated. This exercise indicated that Q_{imb} could be underestimated for approximately 50 lakes. Collectively one fifth of the lakes (at minimum) likely have poorly characterized runoff; given uncertain atmospheric deposition, runoff estimates for many more lakes may not be well established.

3.4. Critical load exceedance

Comparison of CL(A) with the anticipated increment in S deposition through 2020 suggested that exceedance will occur despite very low S deposition. Median probability of S deposition exceeding the CL(A) was 3 and 11%, for default and alternate ANC_{limit}, respectively (Fig. 7). Uncertainty in CL(A) was very low among the most acid-sensitive lakes (Fig. 5), and the majority of the cumulative distribution function for exceedance (excepting for the least sensitive lakes) is very steep (Fig. 7). Consequently a small error in S deposition (on the order of a few $mmol_c\ m^{-2}\ yr^{-1}$) would lead to dramatic differences in the apparent risk of acidification.

It is important to note here that while exceedance was predicted for a small percentage of the lakes, the deposition used in these calculations reflects a small (5%) proportion of current deposition levels. Exceedance levels would be higher if all deposition rather than the potential increment through the year 2020 was considered. Moreover, total S deposition at the most remote atmospheric deposition monitoring station in Canada (Snare Rapids, NWT) is approximately 2 $mmol_c\ m^{-2}\ yr^{-1}$ which corresponds with the 5th percentile CL(A) (default ANC_{limit}). The frequency of extremely low calculated CL(A) (all approaches) among the study lakes might suggest that increases in S deposition should be avoided in this region. Nonetheless, as little of the modeled S deposition appears in the lakes, it is necessary to question the appropriateness of the SSWC for identifying CL(A) in this region.

The SSWC is premised on the basis of a long-term steady-state which assumes that S is mobile, thus no sinks of S are characterized. It is clear, however, that S retention occurs under current conditions; median retention among the 246 catchments acting as sinks of S was approximately 80% of modeled S deposition. Peatlands are an important feature of the landscape in the region, and exhibit the potential to store elements including C, S and N over (long-term) time scales relevant in the context of the steady-state critical load approach. In the case of S, long-term storage capacity reported for peatlands (Novak et al., 2005) is comparable to current S deposition at the study sites. Accordingly, CL(A) may be underestimated according to current methods. This shortcoming could be addressed by adapting the First-order Acidity Balance (Henriksen and Posch,

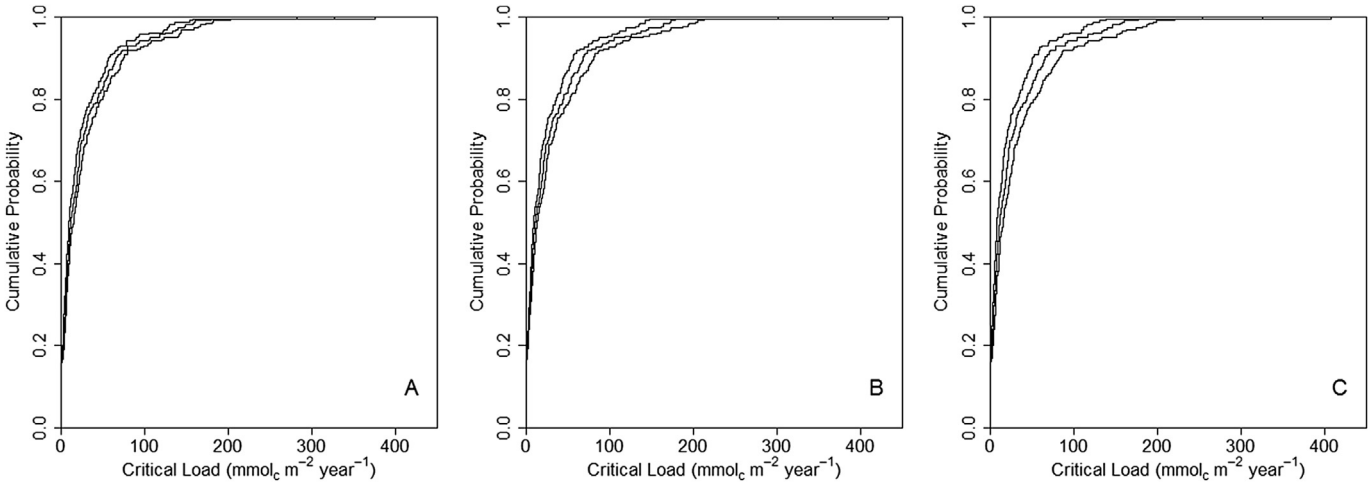

Fig. 5. Uncertainty in critical loads of acidity (CL(A)) due to (A) base cation concentrations, (B) isotope mass balance based runoff estimates, and (C) combined uncertainty attributed to both base cations and runoff estimates. Lines shown represent the 5th, 50th and 95th percentiles according to the alternate ANC_{limit}.

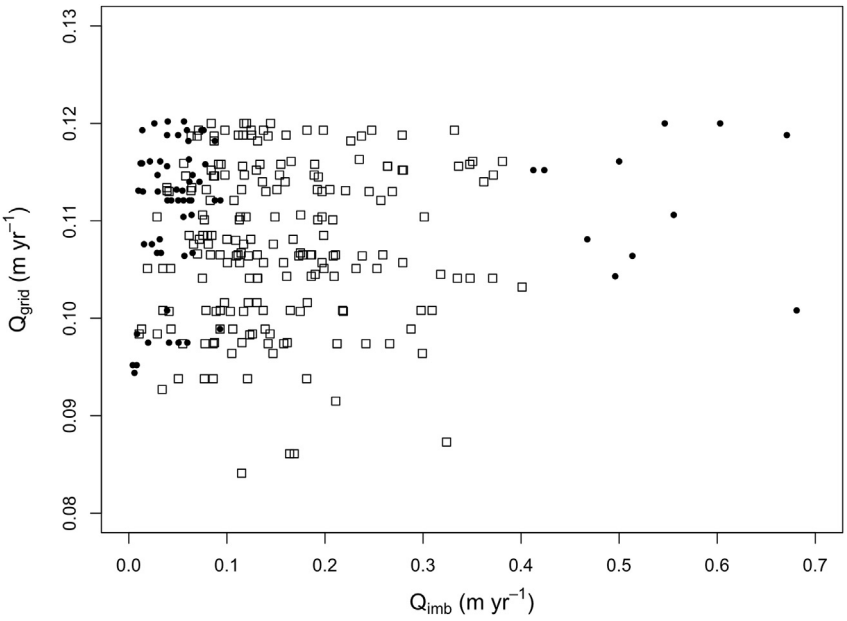

Fig. 6. Comparison of runoff estimates from grid-based (Q_{grid}) and isotope mass balance (Q_{imb}) estimates. Open squares denote Q_{imb} estimates that are consistent with current understanding of precipitation amount and atmospheric deposition levels to the catchments. Filled circles indicate Q_{imb} estimates that may over or underestimate runoff amount.

2001) steady-state critical load approach to account for S retention. The model structure could be modified to improve estimates of CL(A) by including long-term S retention terms (in organic soils) to complement existing terms for S (in-lake) and N (terrestrial). Dynamic biogeochemical models could alternately be used to investigate the potential for temporal changes in surface water chemistry in the region in response to changing atmospheric deposition and climate. This approach could prove useful for illustrating how S pools may change over the long-term, as catchment budgets in eastern North America have indicated that S retained and stored during several decades of elevated deposition is being released under conditions of reduced S deposition, with strong dependence of S export on drying and wetting cycles (Mitchell et al., 2011). While acid deposition in the region considered herein has not been elevated over a sustained period, the capacity for long-term S storage in the study catchments nonetheless remains a key uncertainty. Additional data are necessary to improve steady-state CL(A) estimates (e.g. FAB) or simulate dynamic response of surface waters in the region. Improved understanding of catchment processes, including S storage mechanisms, and greater certainty in hydrological fluxes and atmospheric deposition levels of S, N, BC and Cl in the region will be a valuable asset for assessing acidification risk.

4. Conclusions

In acidification studies across Canada, the SSWC model has typically been applied in an off-the-shelf manner with selection of the ANC_{limit} often being the only local consideration. For this group of headwater boreal lakes in northwestern SK, such a conventional application is not well-suited. The empirical relationship between SO_4 and BC used in a chain of equations in the model is not consistent with observations and no regionally relevant regression was found that could be used in its place. In this region, where S

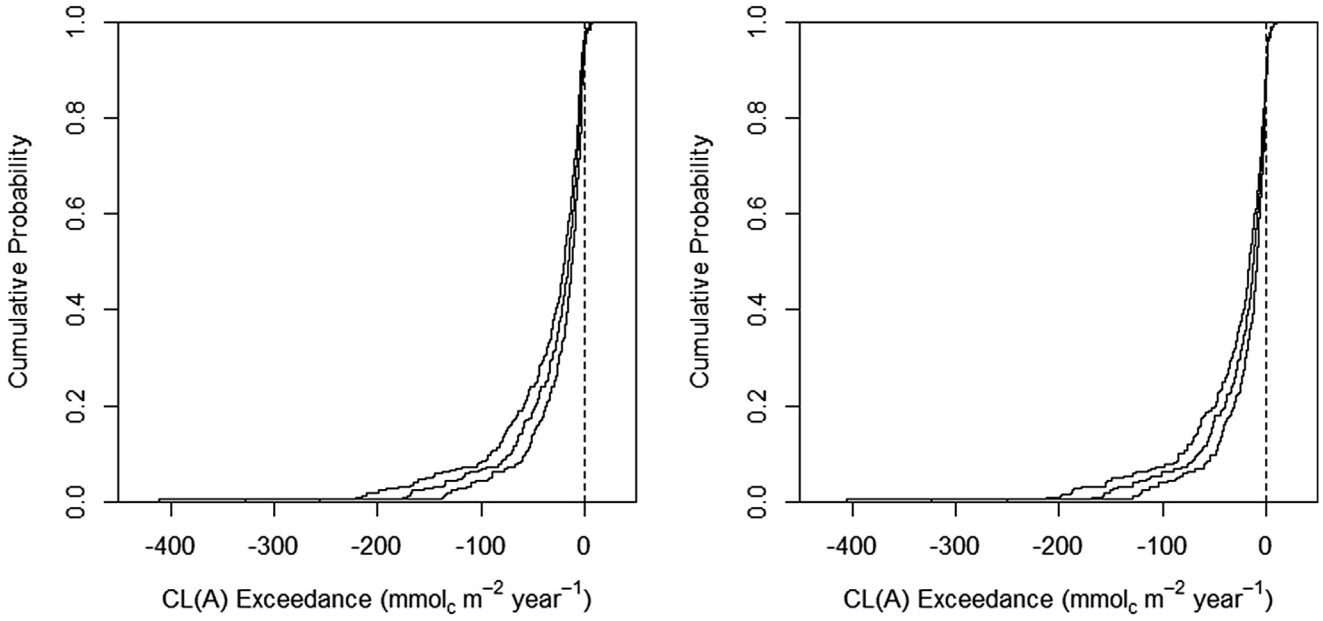

Fig. 7. Critical load exceedance for the study lakes according to uncertainty based Baseline CL(A) and estimated increase in sulphur deposition through 2020 (see text for details). Standard ANC_{limit} (left panel) and alternate ANC_{limit} (right panel) are shown, and the broken line indicates transition from conditions of non-exceedance (negative values) to exceedance (positive values) of the CL(A). Lines shown represent the 5th, 50th and 95th percentile CL(A) exceedance.

deposition remains low and lakes are unlikely to have undergone notable shifts in chemistry associated with atmospheric deposition, a modified version of the SSWC that uses current [BC^*] rather than an estimated historical condition was used to calculate CL(A). This baseline approach should be favoured for lakes that reflect a relatively undisturbed state, as it is simpler and eliminates reliance on empirical relationships for other regions (which may not be applicable to the region of interest). The baseline approach to CL(A) determination is however dependent on reliable estimates of atmospheric deposition, as these data are used to quantify sources of SO_4 and Cl. For the region in question, accurate atmospheric deposition information is also necessary for improved understanding of hydrological behaviour of the catchments as currently available catchment-based runoff estimates do not instill confidence in all cases. Given that CL(A) are often low and in close balance with acid deposition for many of the study lakes, improved understanding of atmospheric deposition would contribute to enhanced characterization of acidification risk in this region. Coupling of lake and deposition data also indicate that S is strongly retained in many catchments, and therefore CL(A) may be underestimated should long-term S storage be occurring in peatlands.

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